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Partial Pressures and High-Temperature Thermodynamic Properties for the Germanium-Tellurium System

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Abstract

Our earlier optical density measurements over $\mathrm{Ge-Te}$ compositions are reanalyzed. Spectral characteristics of the $\mathrm{GeTe(g)}$ spectrum are determined from measurements with a 1 at.% Te sample near 1200 K. Beers law constants for $\mathrm{GeTe(g)}$ are established by requiring consistency between spectroscopic results for the dissociation of $\mathrm{GeTe(g)}$ into $\mathrm{Ge(g)}$ and $\mathrm{Te_2(g)}$ and our description in terms of the partial pressure of $\mathrm{Te_2}$ and the partial optical density of GeTe over Ge saturated $\mathrm{GeTe(c)}$. Between 870 and 997 K the partial pressures over Ge saturated $\mathrm{GeTe(c)}$ are $\ln \mathrm{P(Te_{2,atm})} = -24{,}800/\mathrm{T} + 17.600$ and $\ln \mathrm{P(GeTe,atm)} = -23{,}900/\mathrm{T} + 19.400$. The latter pressure is about 2.5 times lower than our earlier result. Between 869 and 997 K the Gibbs energy of dissociation of $\mathrm{GeTe(g)}$ to $\mathrm{Ge(g)}$ and $\mathrm{Te_2(g)}$ is $\Delta G_D^o = 281{,}254 - 53.59\mathrm{T}$ J/mol while the Gibbs energy of formation of Ge saturated $\mathrm{GeTe(c)}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ is $\Delta G_f^o = -44{,}994 + 26.978\mathrm{T}$ J/mol. The partial pressures along and within the three phase curve of $\mathrm{GeTe(c)}$ and along the three phase curve for $\mathrm{Ge(c)}$ are determined and discussed. Comparisons with other types of data are made.

Introduction

Knudsen cell measurements of the partial pressure of $GeTe(g)$ over the high-temperature $GeTe(c)$ phase differ by as much as a factor of four.[1,2,3,4,5] The standard Gibbs energy of formation for this phase has been determined only at low temperatures where the crystal structure is different. There are two extreme versions for the homogeneity range of the high-temperature $GeTe(c)$ phase. Both agree that the homogeneity range extends to about 51 at.% Te, i.e. is about 1 at.% wide. However, in one version,[6] based mainly on the chemical analysis of the first and last to freeze portions of directionally frozen ingots, the maximum melting point is at 50.60 at.% Te and the solidus on the Ge side of the maximum melting point lies at compositions greater than 50 at.% Te. In the other,[7,8] the maximum melting point is between 49.84 and 50.00 at.% Te and is at 997 K. Because of these inconsistencies we reexamine our optical density measurements made some time ago. Previously, we depended upon Knudsen cell measurements[1,2] to establish the Beers law constants required to convert optical densities to partial pressures of $GeTe(g)$. Now we construct the partial optical densities of $Te_2(g)$ and $GeTe(g)$ and apply them to the gaseous dissociation of $GeTe(g)$. This fixes the enthalpy of dissociation and, by comparison with the spectroscopic result for the entropy of dissociation,[12] the Beers law constants for $GeTe(g)$. The resulting partial pressure of $GeTe(g)$ is about one half of that obtained before[7] and about the average of those determined by Knudsen cell measurements. However, as discussed above, its value is independent of the Knudsen cell measurements.

The same measurements are used to obtain a standard Gibbs energy of formation of Ge saturated $GeTe(c)$ first from $Ge(c)$ and $Te_2(g)$ and then from $Ge(c)$ and $Te(l)$. Standard values at 298 K for the enthalpy and entropy of formation are obtained. Least squares fits of the $Te_2(g)$ partial pressures for a number of compositions within the $GeTe(c)$ homogeneity range are tabulated. Values for the partial pressure of tellurium along the three phase curve and for compositions near 50 at.% Te are shown in graphical form and their implications for the high-temperature portion of the phase diagram discussed. The variation of the Gibbs energy of formation of $GeTe(c)$ from $Ge(c)$ and $Te(l)$ is calculated across the compound's homogeneity range using the Gibbs–Duhem relation to obtain the partial pressure of $Ge(g)$. The variation of the partial pressure of $GeTe(g)$ across the homogeneity range of $GeTe(c)$ is also obtained starting with the Gibbs–Duhem relation written in term of $GeTe(g)$ and $Te_2(g)$ as well as from the partial optical density of $GeTe(g)$. Agreement between the two types of calculation for 50 at.% Te justifies the use of the pressures from the partial optical densities to calculate the enthalpy of fusion.

Experimental

The experimental details given in the original publications[7,8] are summarized here. The path lengths of the 2 cm diameter optical cells were measured to the nearest .1 mm and were between 9.0 and 10.0 cm. The cells had a 20 cm long sidearm attached at right angles and near their mid-point. Samples resided at the far end of the sidearm. The optical cell was placed in the sample beam of a reversed optics, double beam, Cary 14H spectrophotometer. Measurements were made with the optical cell at 1273 K and the sample sidearm at a series of lower temperatures ranging from about 700 K to about 1030 K. One exceptional sample containing 1 at.% Te was measured in early studies using a Cary 11 normal optics, double beam spectrophotometer. Filters transparent between about 270 and 500 nm were placed at the end of the sample beam furnace to reduce the amount of furnace radiation reaching the photomultiplier detector. Measurements were taken with sample temperatures as high as 1250 K.

The samples were synthesized from zone refined 5-9 Te and 30 O-cm Ge. The elements were each weighed to the nearest mg to make up a ten gm total weight and heated for 3-6 min at 1213-1253 K in an evacuated, previously outgassed silica tube. They were then quenched in water. The samples were crushed with a boron carbide mortar and pestle to pass a 1 mm opening sieve. They were then sealed off in a previously outgassed

optical cell and annealed for 245 h at 788 K before starting measurements. Sample compositions were 1.00, 49.84, 49.92, 50.00, 50.08, 50.30, 50.60, 50.70, 50.85, 51.01, and 51.50 at.% Te.

Analysis

Partial Optical Densities

Since the temperature of measurement is high and the pressures relatively low, we assume that the vapor is ideal. The partial pressure of $GeTe_2$ is about one-tenth that of Te_2 [3] and is neglected. The optical density at a wavelength, $D_{\lambda,j}$ is assumed to be the sum of partial optical densities of $Te_2(g)$ and $GeTe(g)$, $D_T(\lambda, j)$ and $D_G(\lambda, j)$. One then has,

$$D_{\lambda 1} = D_T(\lambda 1) + D_G(\lambda 1)$$
$$D_{\lambda 2} = D_T(\lambda 2) + D_G(\lambda 2)$$

(1)

It is also assumed that the wavelengths are chosen so that a partial optical density and its corresponding partial pressure are proportional. This implies that one can define constants k and m,

$$D_T(\lambda 2)/D_T(\lambda 1) = m \text{ and } \frac{D_G(\lambda 1)}{D_G(\lambda 2)} = k$$

(2)

With Eq 2 one can solve Eq 1 for each partial optical density as,

$$D_T(\lambda 1) = \frac{D_{\lambda 1} - kD_{\lambda 2}}{1 - km} \text{ and } D_T(\lambda 2) = m\frac{(D_{\lambda 2} - mD_{\lambda 1})}{1 - km}$$

(3)

$$D_G(\lambda 2) = \frac{D_{\lambda 2} - mD_{\lambda 1}}{1 - km} \text{and } D_G(\lambda 1) = k\frac{(D_{\lambda 2} - mD_{\lambda 1})}{1 - km}$$

(4)

Equations 3 and 4 give each partial optical density as a function of the total measured optical densities at two wavelengths and the form factors k and m for the T and G spectra. In practice one would choose $\lambda 1$ where T absorbs strongly and G weakly and $\lambda 2$ oppositely. In the simplest case the absorption at $\lambda 1$ is all due to T and that at $\lambda 2$ is all due to G, then k and m are zero and Eq 3 and 4 show each partial optical density is equal to the total optical density at its absorbing wavelength. In our calculations we take $T = Te_2$ and generally $\lambda 1 = 435.7nm$ where Te_2 absorbs strongly and $GeTe$ weakly. In addition, $G = GeTe(g)$ and λ2=320 or 330 nmλ2=320 or 330 nm, where $GeTe$ absorbs strongly and Te_2 weakly. If the optical density at 435.7 nm is greater than about three and too large to be measured the optical density at 500 nm is used, λ1=500 nmλ1=500 nm. The constants m in Eq 2 for $T = Te_2$ are listed in Table 1 and are obtained from extensive measurements on the vapor in equilibrium with pure Te(c,l). The Beers law constants are also determined in the same experiments by comparison with the published vapor pressure at one temperature. They give the partial pressure of Te_2 in terms of the partial optical density of Te_2 at a given wavelength and optical path length, L, as,

$$\mathrm{P_{Te_2}(atm)} = \frac{\alpha_{\mathrm{Te_2},\lambda}\mathrm{D_{Te_2}}(\lambda)}{\mathrm{L}}$$

(5)

To characterize $\mathrm{GeTe(g)}$, measurements were made with a 1 at.% Te sample between 1180 and 1220 K and between 320 and 435.7 nm. The optical densities fell along parallel curves consistent with the assumption of a single absorber. The value of the optical density at 320 nm was 7.4 times that of the optical density at 435.7 nm. As seen in Table 1 this indicates $\mathrm{Te_2(g)}$ was a minor component under these conditions and the spectrum was essentially that of $\mathrm{GeTe(g)}$. For $\mathrm{Te_2}$ the table shows that, in contrast, the optical density at 320 is only .0187 that 435.7 nm. The partial pressure of $\mathrm{GeTe(g)}$ is given by an equation analogous to Eq 5,

$$\mathrm{P_{GeTe}(atm)} = \alpha_{\mathrm{GeTe},\lambda}\mathrm{D_{GeTe}}(\lambda)/\mathrm{L}$$

(6)

The Beers law constants for GeTe are discussed in the next section. The wavelength pairs used to calculate the partial optical densities of $\mathrm{Te_2(g)}$ were 435.7-320.0, and 435.7-330 nm. For the first pair of wavelengths the partial pressures are given by the equations:

$$\mathrm{P_{Te_2}} = .0316(1.002)(\mathrm{D_{435.7}} - .117\mathrm{D_{320.0}})/\mathrm{L}$$

$$\mathrm{P_{GeTe}} = .1398(1.002)(\mathrm{D_{320.0}} - .0187\mathrm{D_{435.7}})/\mathrm{L}$$

(7)

where the pressure is in atm and the path length in cm.

Table 1 Spectrum constants and Beers law constants for $\mathbf{Te_2(g)}$ and $\mathbf{GeTe(g)}$

λ, nm	310.0	320.0	330.0	365.0	435.7	500.0
$\mathrm{Te_2}$ D_λ=D435:7	.010	.0187	.0278	.492	1.0	.088
α_λ; atm-cm					.0316	.1485
GeTe $D_{435:7}=D_\lambda$	.0788	.117	.152	.329	1.0	2.0
α_λ; atm-cm	.103	.153	.198	.360		

Vapor Phase Dissociation and Beers Law Constants of $\mathrm{GeTe(g)}$

As the first step in the determination of the Beers law constants of $\mathrm{GeTe(g)}$ we consider the gaseous dissociation of $\mathrm{GeTe(g)}$,

$$\mathrm{GeTe(g)} = \mathrm{Ge(g)} + \frac{1}{2}\mathrm{Te_2(g)}$$

(8)

At equilibrium the chemical potential of $\mathrm{GeTe(g)}$ must equal the sum of those of $\mathrm{Ge(g)}$ and one-half that of $\mathrm{Te_2(g)}$. Assuming an ideal gas phase and gathering all the partial pressures on one side, one has,

$$\mathrm{RT\ ln\ (P_{Ge}P_{Te_2}^{1/2}/P_{GeTe})} = \mu^{\mathrm{o}}_{\mathrm{GeTe(g)}} - \mu^{\mathrm{o}}_{\mathrm{Ge(g)}} - (1/2)\mu^{\mathrm{o}}_{\mathrm{Te_2(g)}} = -\Delta\mathrm{G^o_D} = -\Delta\mathrm{H_D} + T\Delta\mathrm{S_D}$$

(9)

The left side of this equation is now developed. The partial pressure of Te_2 for the 1 at.% Te sample G31 and the 49.84 at.% Te sample G1B are shown in Fig. 1 on a logarithmic scale as a function of the reciprocal temperature of the sample. They agree within experimental error as they should since below 997 K these compositions fall within the same $\mathrm{Ge(c)}$-Ge-saturated $\mathrm{GeTe(c)}$-vapor field. A least squares fit between 1.15 and 1.002 in 1000/T gives,

$$\ln \mathrm{P}_{\mathrm{Te}_2}(\mathrm{atm}) = -24{,}800 \pm 700/\mathrm{T} + (17.6 \pm .8)$$

(10)

where the 95% confidence limits are given following the plus–minus signs.

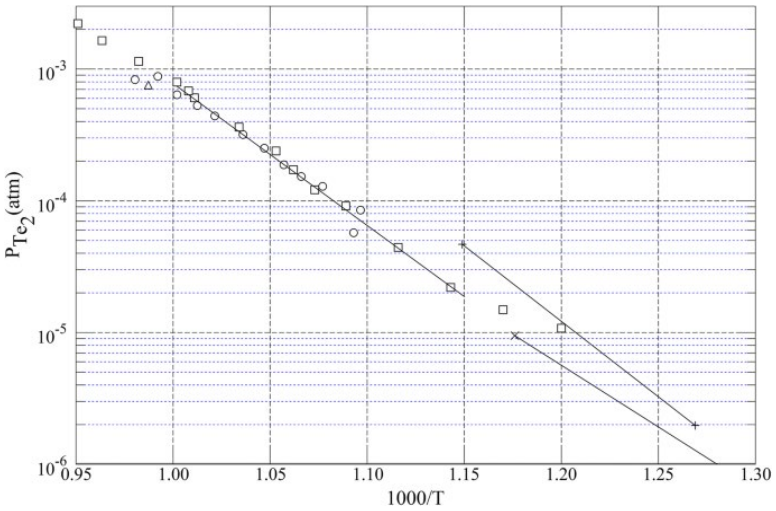

Fig. 1 Partial pressure of Te_2 over Ge-saturated $\mathrm{GeTe(c)}$. G31, 1 at.% Te. Circles, pressure determined from optical densities at 435.7 and 320 nm pair. G1B, 49.84 at.% Te. Squares: 435.7-320 nm. Line through points is a least squares fit given by Eq 10. Two lines at lowest temperatures are mass spectrograph-Knudsen cell measurements from Ref 3, upper line, and Ref 4 lower line

The standard deviation of the fit to ln P versus 1000/T for 41 points is .09. For comparison the partial pressures of Te_2 obtained in two mass spectrograph-Knudsen cell studies[3,4] are also shown in Fig. 1. An extension of our line falls close to the line for Molchanov et al.,[4] whose upper limit is terminated by an X. The solubility of Te in $\mathrm{Ge(c)}$ is one percent or less[9] so that the partial pressure of $\mathrm{Ge(g)}$ in Eq 9 equals that of pure $\mathrm{Ge(c)}$ to within the same percentage. In the 600-1200 K range a fit to the vapor pressure data for $\mathrm{Ge(c)}$ in Hultgren et al.[10] gives,

$$\ln \mathrm{P}^{\mathrm{o}}_{\mathrm{Ge}} = -45{,}289.3/\mathrm{T} + 17.0261$$

(11)

Finally, the partial optical density of $\mathrm{GeTe(g)}$ is calculated for samples G31, 1.00 at.% Te at 320 and 330 nm, and G1B, 49.84 at.% Te at 320 nm. In each case the $\mathrm{Te}_2\mathrm{(g)}$ contribution is obtained from the optical density at 435.7 nm. Using the data in Table 1 the partial optical densities are then normalized to their values for the 320-435.7 wavelength pair,

$$\mathrm{D}_{\mathrm{GeTe}}(\mathrm{normalized\ to\ 320nm, 1cmpath})$$

$$= \begin{cases} 1.00(1.002)(\mathrm{D}_{320} - .0187\mathrm{D}_{435.7})/\mathrm{L} \\ 1.294(1.004)(\mathrm{D}_{330} - .0278\mathrm{D}_{435.7})/\mathrm{L} \end{cases}$$

(12)

The results are shown in Fig. 2. There is good agreement among the points from different samples as well as among different wavelength pairs for a given sample. A least squares fit to the logarithm between 1.20 and 1.00 in 1000/T gives,

$$\ln \mathrm{D}_{\mathrm{GeTe}}(\text{normalized to 320 nm, 1 cm path}) = -23{,}867 \pm 503/\mathrm{T} + (21.2830 \pm .538)$$

(13)

The standard deviation for the fit to 44 points is .087. The partial pressure of GeTe is obtained by multiplying the normalized optical density by the Beers law constant for 320 nm.

$$\ln \mathrm{P}_{\mathrm{GeTe}} = \ln \alpha_{\mathrm{GeTe},320} + \ln \mathrm{D}_{\mathrm{GeTe}}(320 \text{ nm}, 1 \text{ cm path})$$

(14)

Substituting Eq 10 through 14 for the left side of Eq 9 then equating the constant terms to $-\Delta H_D$ and the sum of the terms multiplying T to ΔS_D gives,

$$\Delta \mathrm{H}_{\mathrm{D}} = -8.3145(-45{,}289.3 - 0.5 \times (24{,}810) + 23{,}867) = 281{,}254\mathrm{J/mol}$$

(15)

and

$$\Delta \mathrm{S}_{\mathrm{D}} = \begin{cases} 53.59 \\ 8.3145\big(17.0261 + 0.5(17.6489) - 21.2830 - \ln \alpha_{320,\mathrm{GeTe}}\big) \end{cases}$$

(16)

Here 53.9 is a known value independent of the present study. Our earlier analysis[7] had this entropy change equal to 58.59 in agreement with Kelley.[12] This value was obtained using molecular constants derived from spectroscopic studies. Subsequently, the ground state of Te(g) has been found[11] to be non-degenerate rather than triply degenerate so that the entropy of $\mathrm{Te}_2(\mathrm{g})$ must be corrected by − Rln3, resulting in the value shown in Eq 16. Solving for the Beers law constant in Eq 16 gives

$$\alpha_{320,\mathrm{GeTe}} = 0.153,$$

(17)

the value shown in Table 1. The Beers law constants for the other wavelengths shown in Table 1 follow from the optical density ratios given there. With Eq 13 and 17 the partial pressure of $\mathrm{GeTe(g)}$ over Ge-saturated $\mathrm{GeTe(c)}$ is,

$$\ln(\mathrm{P}_{\mathrm{GeTe}}) = -23{,}900 \pm 500/\mathrm{T} + (19.400 \pm .500)$$

(18)

The heat of vaporization follows as 198,442 J/mol. The value for the partial pressure of GeTe over Ge-saturated $\mathrm{GeTe(c)}$ along with literature values obtained from Knudsen cell measurements and mass spectrograph-Knudsen cell measurements is shown in Fig. 3. Our values, shown by the dashed line terminated by diamonds, are about the average of these but has been obtained independently of them. They extend almost exactly into the result of Hirayama[1] and fall almost on top of those from Lyubimov et al.[5] Although the partial pressures in Fig. 3 spread over a range of about 4.5 their slopes are essentially the same. Finally, using Eq 15 and 16, the Gibbs energy for the dissociation of $\mathrm{GeTe(g)}$ in Eq 9 can be written as,

$$\Delta \mathrm{G}_{\mathrm{D}}^{\mathrm{o}} = 281{,}254 - 53.59\mathrm{TJ/mol}$$

(19)

Equation 9 then becomes:

$$\mathrm{P_{Ge}P_{Te_2}^{\frac{1}{2}}/P_{GeTe}} = \mathrm{EXP}(-33{,}827/\mathrm{T} + 6.4454)$$

(20)

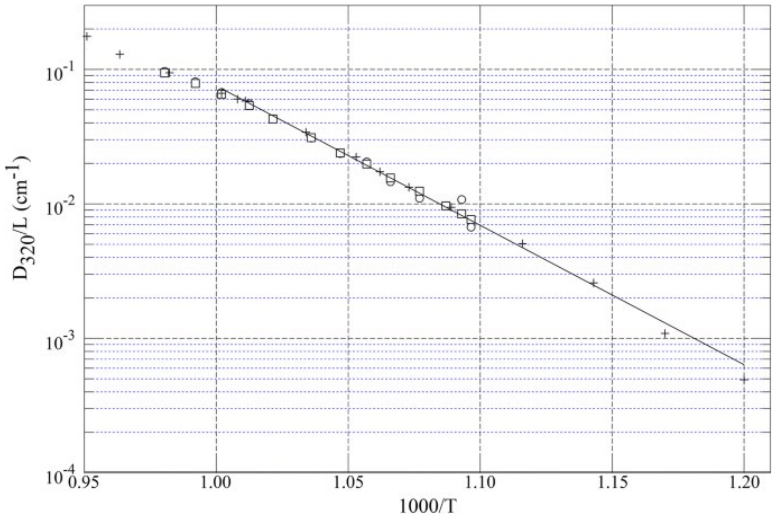

Fig. 2 Partial optical density of GeTe over Ge-saturated $\mathrm{GeTe(c)}$ for one cm path at 1000 °C and normalized to 320 nm. G31 1 at.% Te, circles 320-435.7, squares 330-435.7. G1B 49.84 at.% Te, crosses 320-435.7. Line is a least squares fit to data from 1.20 to 1.002 in 1000/T given by Eq 13

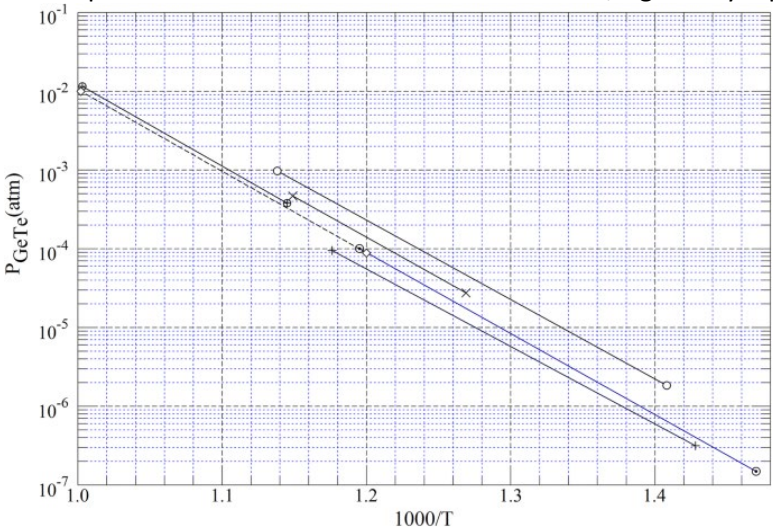

Fig. 3 Partial pressure of GeTe over Ge-saturated $\mathrm{GeTe(c)}$ from the literature and our value shown as a dashed line terminated by diamonds. The symbols show the limits of the temperature range for each measurement. The circles from Ref 2, X's from Ref 3, high-temperature circled cross from Ref 5, bull's-eyes from Ref 1, and crosses from Ref 4. The X's from Ref 3 and crosses from Ref 4 are mass spectrograph-Knudsen cell measurements in which the pressures of $\mathrm{Te_2}$ and $\mathrm{GeTe_2}$ are also measured

Application

Partial Pressures of $\mathrm{Te_2}$ and GeTe in Equilibrium with $\mathrm{Ge(c)}$ at High Temperature

The above developments for the gaseous dissociation of $\mathrm{GeTe(g)}$ below 997 K can be applied to equilibrium between $\mathrm{Ge(c)}$ and $\mathrm{Ge-Te}$ liquid between 997 K and the melting point of $\mathrm{Ge(c)}$. Using Eq 11 for the vapor pressure of Ge in Eq 20 as well as experimental values for the partial pressure of $\mathrm{GeTe(g)}$ then solving for the partial pressure of $\mathrm{Te_2}$ gives

$$\mathrm{P_{Te_2}} = \mathrm{P_{GeTe}^2 EXP(22{,}924.6/T + 21.1614)}$$

(21)

The partial pressures of GeTe for temperatures greater than 997 K and the corresponding partial pressures of $\mathrm{Te_2}$ are shown in Fig. 4. Points calculated with Eq 21 are shown as Maltese crosses and generally are in good agreement with those obtained directly from the partial optical density of $\mathrm{Te_2}$.

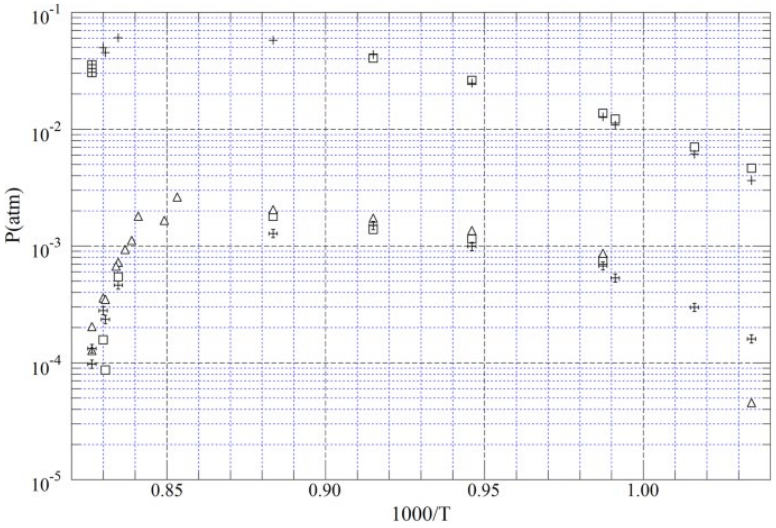

Fig. 4 Upper set of symbols are the partial pressure of germanium telluride while the lower set are that of diatomic tellurium over Te-saturated $\mathrm{Ge(c)}$ at high temperatures. Data obtained with a 1.00 at.% Te sample. The partial pressures are derived from the 435.7-320.0 nm pair shown as squares and from the 4357-365.0 nm pair shown as crosses. Partial pressures of $\mathrm{Te_2}$ calculated from those of $\mathrm{GeTe(g)}$, $\mathrm{Ge(c)}$, with Eq 21 are shown as Maltese crosses

Gibbs Energy of Formation of Ge-Saturated $\mathrm{GeTe(c)}$

We now consider the reaction:

$$\mathrm{Ge(c)} + \frac{1}{2}\mathrm{Te_2(g)} \rightleftharpoons \mathrm{GeTe(Ge-satd\ c)}$$

(22)

At equilibrium the sum of the chemical potentials of the reactants equals that of the product,

$$\mu_{\mathrm{Ge(c)}} + \frac{1}{2}\mu_{\mathrm{Te_2(g)}} = \mu_{\mathrm{GeTe(Ge-satd\ c)}}$$

(23)

Assuming the vapor is ideal and again taking advantage of the fact that the solubility of Te in $\mathrm{Ge(c)}$ is under 1 at.%, so that the chemical potential of germanium is essentially that of pure germanium, Eq 23 can then be written as,

$$\mu^{\mathrm{o}}_{\mathrm{Ge(c)}} + \frac{1}{2}\mathrm{RT}\ln\left(\mathrm{P_{Te_2}}\right) + \frac{1}{2}\mu^{\mathrm{o}}_{\mathrm{Te_2}} = \mu_{\mathrm{GeTe(Ge-satd\ c)}}$$

(24)

where $\mu^{\mathrm{o}}_{\mathrm{Ge(c)}}$ is the chemical potential of pure germanium crystal and $\mu^{\mathrm{o}}_{\mathrm{Te_2}}$ is the chemical potential of $\mathrm{Te_2(g)}$ at one atm pressure. Rearranging to solve for the pressure gives,

$$\frac{1}{2}\mathrm{RT}\ln \mathrm{P_{Te_2}} = \mu_{\mathrm{GeTe(Ge-satd\ c)}} - \mu^{\mathrm{o}}_{\mathrm{Ge(c)}} - \frac{1}{2}\mu^{\mathrm{o}}_{\mathrm{Te_2(g)}} = \Delta \mathrm{G}^{\mathrm{o}}_{\mathrm{f1}}$$

(25)

Using Eq 10 for the natural logarithm of the tellurium pressure over Ge-saturated $\mathrm{GeTe(c)}$ gives the Gibbs energy change for the equilibrium of Eq 22 as,

$$\Delta \mathrm{G}^{\mathrm{o}}_{\mathrm{f1}} = -(103{,}000 \pm 4000) + (73.4 \pm .3)\mathrm{TJ/mol}$$

(26)

The standard Gibbs energy of formation of Ge-saturated $\mathrm{GeTe(c)}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ can be obtained from Eq 25. First one considers the equilibrium between pure tellurium liquid and $\mathrm{Te_2(g)}$. In terms of chemical potentials this equilibrium is,

$$\mu_{\mathrm{Te(l,x=1)}} = \frac{1}{2}\mathrm{RT}\ln\left(\mathrm{P^{o}_{Te_2}}\right) + \frac{1}{2}\mu^{\mathrm{o}}_{\mathrm{Te_2}}$$

(27)

Solving for the last term in Eq 27 and using the solution to eliminate that term in Eq 25 gives, after rearrangement to gather the pressure terms on the left,

$$\frac{1}{2}\mathrm{RT}\ln\left(\mathrm{P_{Te_2}/P^{o}_{Te_2}}\right) = \mu^{\mathrm{o}}_{\mathrm{GeTe(Ge-satd\ c)}} - \mu^{\mathrm{o}}_{\mathrm{Ge(c)}} - \mu^{\mathrm{o}}_{\mathrm{Te(l,x=1)}} = \Delta \mathrm{G}^{\mathrm{o}}_{\mathrm{f,2}}$$

(28)

It has been shown[13] that the piece-wise equations which have been given for the vapor pressure of $\mathrm{Te(l)}$ and which account for the sudden rise in the vapor pressure as the melting point is approached from above can be well approximated by,

$$\ln \mathrm{P^{o}_{Te_2}} = 10.1522 - 12123/\mathrm{T} - 847793.87/\mathrm{T}^2$$

(29)

This equation is used in the following way. For each $\mathrm{T} - \mathrm{RT}\ln\left(\mathrm{P}_{\mathrm{Te}_2}\right)$ pair in the data set for Ge saturated $\mathrm{GeTe(c)}$ a value for $\mathrm{RT}\ln\left(\mathrm{P}^{\mathrm{o}}_{\mathrm{Te}_2}\right)$ from Eq 29 is added and the left hand member of Eq 28 formed. This new data set is then subjected to a least squares fit. The result is,

$$\Delta \mathrm{G}^{\mathrm{o}}_{\mathrm{f2}} = -44{,}994. + 26.978\mathrm{T\,J/mol},$$

(30)

for the formation of Ge-saturated $\mathrm{GeTe(c)}$ from the condensed elements,

$$\mathrm{Ge(c)} + \mathrm{Te(l)} = \mathrm{GeTe(Ge - satd\ c)}$$

(31)

The midpoint of the temperature range of measurement for the standard Gibbs energy of formation of Ge-saturated $\mathrm{GeTe(c)}$ given by Eq 30 is 929 K where the enthalpy of formation is − 44,994 J/mol and the entropy change is − 26.978 J/mol-K.

Standard Enthalpy and Entropy of Formation for Ge Saturated $\mathrm{GeTe(c)}$ at 298 K and Comparison with Other Results

The enthalpy and entropy of formation at 298 K are of interest for comparison with other measurements. However, a complicating factor arises because with decreasing temperature the high-temperature rocksalt, *β*, form of $\mathrm{GeTe(c)}$ starts to transform for less Te rich compositions to an *α*, orthorhombic form at about 703 K and at 675 K to a *γ*, rhombohedral, phase for the more Te rich compositions.[14,15] According to Ref 14 the *α* form is stable between about 50.1 and 50.4 at.% Te and the *γ* form between about 50.6 and 51.4 at.% Te so a *α* + *γ* two phase region about .2 at.% wide exists. In many studies the composition of the $\mathrm{GeTe(c)}$ used is not given.

The standard enthalpy and entropy of formation of Ge saturated $\mathrm{GeTe(c)}$ at 298 K corresponding to the Gibbs energy of Eq 30 and equilibrium of Eq 31 were obtained using the heat capacities of $\mathrm{Ge(c)}$ and Te(c,l) given by SGTE[16] for the elements. The heat capacity of $\mathrm{GeTe(c)}$ used is based on a critical examination of available data which was given in a paper on the enthalpy of formation of GeTe by fluorine bomb calorimetry.[17] Recommended values for the heat capacity were given in a table. We have fit these data to a linear equation in T. The result along with the heat capacity of $\mathrm{GeTe(c)}$ relative to the sum of those for $\mathrm{Ge(c)}$ and Te(c,l) are:

$$\begin{aligned} \mathrm{C_P\left(GeTe(c)\right)} &= 42.255 + .0218\mathrm{T} && 298 - 997\mathrm{KJ/mol - K} \\ \Delta \mathrm{C_P} &= -3.1602 + .0098086\mathrm{T} && 298 - 722.6\mathrm{KJ/mol - K} \\ \Delta \mathrm{C_P} &= -195.017 + .3942\mathrm{T} - 1.956(10^{-4})T^2 && 722.6 - 997\mathrm{K} \end{aligned}$$

(32)

The largest term in obtaining the quantities at 298 K is the 17,489 J/mol enthalpy of melting of Te at 722.6 K. The contributions from the heat capacities are − 228 J/mol and − .523 mol-K. No significant contribution from the α−βα−β transition has been reported. The standard enthalpy and entropy of formation of $\mathrm{GeTe(c)}$ obtained are shown in the 1st row of Table 2.

Table 2 Standard enthalpy and entropy of formation of $\mathrm{GeTe(c)}$ at 298 K in J/mol and J/mol-K, respectively

$\Delta H^{o}_{f,298}$	$\Delta S^{o}_{f,298}$	References
- 27,743	- 3.38	Present study, Ge satd GeTe
- 28,200	+ 1.10	Present study, Ge satd GeTe
- 20,000 ± 3000		Flouride bomb calor, Ref [17]
- 56,567	- 4.18	Emf meas., Ref [19]
	+ 9.37, 16.91	Low temp. heat capacity, Ref [20,21]

The quantities at 298 K can be obtained by another route using the same experimental data from this study. One starts with Eq 22 for the chemical attack on $\mathrm{Ge(c)}$ by $\mathrm{Te_2(g)}$ to form Ge saturated $\mathrm{GeTe(c)}$ and Eq 26 for the corresponding Gibbs energy change. The enthalpy and entropy at the mid temperature of about 900 K can be read immediately as − 103,141 J/mol and − 73.371 J/mol-K. To obtain the enthalpy and entropy changes at 298 K for Eq 33 the quantities H900−H298 and S900−S298H900−H298 and S900−S298 for GeTe were obtained using the heat capacity for $\mathrm{GeTe(c)}$ given by the first equation in Eq 32. Those for $\mathrm{Ge(c)}$ were obtained from SGTE[16] and those for $\mathrm{Te_2(g)}$ from a table given in an analysis of the solid–liquid–vapor equilibrium of tellurium.[18] The results are − 109,321 J/mol and − 83.328 J/mol-K for the equilibrium of Eq 22. The corresponding quantities for the formation of $\mathrm{GeTe(c)}$ from solid $\mathrm{Ge(c)}$ and Te(c) at 298 K are obtained by adding the process, $\mathrm{Te(c)} \rightarrow \frac{1}{2}\mathrm{Te_2(g)}$ for which $\Delta H_{298} = 81{,}031 \mathrm{J/mol}$ and $\Delta S_{298} = 84.60 \mathrm{J/mol-K}$. Thus for the formation of Ge saturated $\mathrm{GeTe(c)}$ from solid Ge and Te at 298 one has $\Delta H^{o}_{f} = -28290 \mathrm{J/mol}$ and $\Delta S^{o}_{f} = 1.10 \mathrm{J/mol-K}$. These quantities are shown in the 2nd row of Table 2 and are in fair agreement with those in the 1st row.

A flourine bomb calorimetry study[17] yielded a value of −18.2 ± 4.6 kJ/mol for the standard enthalpy of formation of $\mathrm{GeTe(c)}$ at 298 K. Upon consideration of the data from two other sources the authors arrived at a recommended value of − 20 ± 3 kJ/mol as shown in row 3 of Table 2. One of the sources referred to above is our publication,[8] which gives the Gibbs energy of formation of Ge-saturated $\mathrm{GeTe(c)}$ from its gaseous elements. Since the solubility of Te in $\mathrm{Ge(c)}$ is less than one percent the partial pressure of $\mathrm{Ge(g)}$ can be taken as equal to the vapor pressure of $\mathrm{Ge(c)}$ and only the partial pressure of $\mathrm{Te_2(g)}$ was required to calculate the Gibbs energy of formation. This partial pressure is the same as given here in Eq 10. The authors used our equation for this Gibbs energy in a third law analysis, which requires values for the species entropies, and found the standard enthalpy at 298 K to be − (21 ± 13) kJ/mol. Our values of − 27.5 and − 27.3 kJ/mol shown in Table 2 were of course obtained with a second law analysis.

The 4th row of Table 2 shows values from emf measurements[19] between 553 and 653 K in which the cell reaction involves $\mathrm{GeTe(c)}$ in the presence of Te and therefore presumably GeTe that is as Te-rich as possible i.e. *γ* GeTe. This possibly accounts for the fact that the enthalpy found is much more negative than those from the other measurements.

Low temperature heat capacity measurements give values of 31.09 and 49.50 J/mol-K for the entropy at 298 K of $\mathrm{Ge(c)}$ and Te(c), respectively.[10] Measurements[20] on $\mathrm{GeTe(c)}$ between 53 and 300 K give the entropy at 298 K as 89.96 J/mol-K while measurements[21] between 220 and 460 K give 97.5 J/mol-K. Taking the first value for GeTe gives the positive standard entropy of formation of 9.37 J/mol-K shown in Table 2. Consistency between the standard entropy of formation obtained from low temperature heat capacity measurements and the values derived from our optical density measurements could be achieved if the enthalpy of the high-temperature beta phase were about 9000 J/mol lower than that of the low temperature alpha phase, a situation for which there is no direct evidence as far as we are aware. Powder diffraction measurements[22] in the 400-460 °C range with samples sealed off under vacuum in capillary tubes showed a 1.4% decrease in volume on transformation of the low temperature *α* phase to the higher temperature *β* phase indicating a first order transformation. Thus a non-zero heat of transformation is expected.

Partial Pressures of Te_2 along the Three Phase Curve and Within the $GeTe(c)$ Homogeneity Range

The partial pressures of Te_2 given in our earlier publications[7,8] are only slightly different from those here. Table 3 gives least squares equations for $\ln(P_{Te_2})$ versus $1000/T$ for compositions between 49.84 and 51.50 at.% Te and for pressures that fall within the three phase curve of $GeTe(c)$. We note that for any temperature for which the compositions lie within the three phase field, P_{Te_2} is observed to increase monotonically with the atomic fraction of Te, as required for consistency with the thermodynamic criterion for a stable phase. Figure 5 shows the three phase curve for $GeTe(c)$ on a log P versus 1000/T plot. Besides the compositions defining the three phase curve, the pressures are shown on an expanded scale for five compositions near 50 at.% Te in order that the implications for the structure of the phase diagram near the 997 K melting point of $GeTe(c)$ can be more easily seen. Extensive data that show the intersection of the partial pressures with the three phase line and so define the Te-rich limit for the homogeneity range of $GeTe(c)$ are omitted here but have been tabulated elsewhere.[8]

Table 3 Least squares fits to the partial pressure of diatomic tellurium over $GeTe(c)$

at.% Te	– A	B	σ	Number of points
1.00 and 49.84	24,810 ± 745	17.6489 ± .80	.090	41
49.94	25,809 ± 1800	19.1552 ± 1.6	.08	15
50.00	25,033 ± 60	18.5593 ± .037	.037	14
50.08	22,067 ± 700	15.6575 ± .750	.06	18
50.30	22,865 ± 1210	16.785 ± 1.34	.098	15
50.60	17,261 ± 363	10.9272 ± .40	.03	18
50.70	14,181 ± 800	7.7120 ± .8	.031	11
50.85	13,383 ± 500	7.5367 ± .24	.022	22
51.01	11,638 ± 500	6.1727 ± .52	.019	14

Columns give the composition of the $GeTe(c)$ phase in at.% Te, parameters - A and B in $\ln P_{Te_2} = A/T + B$ with 95% CI, SD, and number of points in the fit. The pressure is in atm and the logarithm is to base e

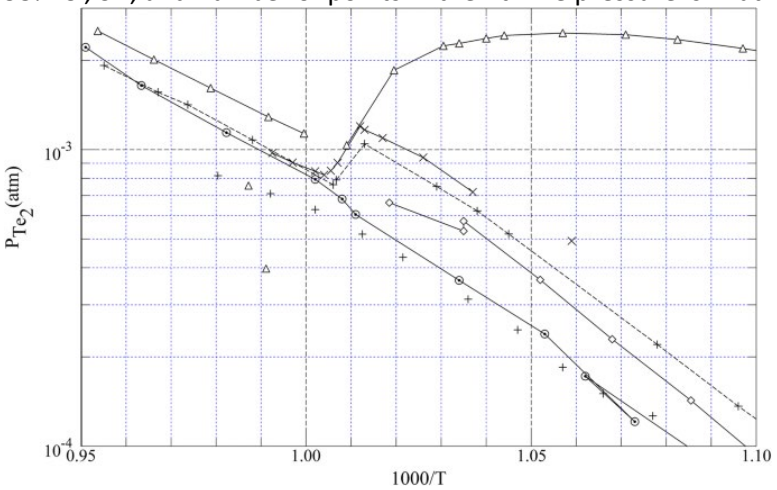

Fig. 5 Partial pressure of Te_2 vs. reciprocal absolute temperature showing the three phase curve for $GeTe(c)$, some features of its internal structure, and the liquid for some compositions. Triangles: 51.50 at.% Te, X's: 50.08, crosses: 50.00, diamonds: 49.92, bull's-eye: 49.84, lower crosses: 1.00 at.% Te

The partial pressures of Te_2 for the 1.00 and 49.84 at.% Te samples shown as the lower set of crosses and the bull's-eyes in Fig. 5 form the Ge-rich leg of the three phase curve along which $Ge(c)$, Ge saturated $GeTe(c)$ and

vapor phase coexist. These have been considered in the determination of the Beers law constants for $GeTe$ in the section 3. The 51.5 at.% Te sample forms the Te-rich leg of the $GeTe(c)$ three phase curve along which $GeTe(c)$ of variable composition, Te rich liquid, and vapor coexist. On a log pressure versus reciprocal temperature plot such as Fig. 5, the pressures for intermediate compositions are generally straight lines within the three phase curve. Their intersections with the three phase curve at their high-temperature end mark solidus temperatures. Their departures from the three phase curve at still higher temperatures mark liquidus temperatures. The partial pressure of 50.08 at.% Te on a log P versus 1000/T plot shows an abrupt change of slope from negative to positive where it intersects the three phase curve in Fig. 5. This indicates the maximum melting composition is less than 50.08. Although the actual intersection is missing for the 50.00 at.% sample this change in slope can be inferred from the fact that the liquid line for 50 at.% lies at pressures below the line for the solid. The change from negative to positive slope indicates that the maximum melting point occurs at less than 50.00 at.% Te. The bull's-eye points for 49.84 at.% change to a more negative slope at about 1000/T = 1.011 (989 K) and then a less negative slope at 1000/T = 1.002 (998 K). This is consistent with this composition intersecting the three phase line at 989 K and then leaving the liquid–solid field to become completely molten at 998 K. The slope for the 1.00 at.% sample abruptly becomes less positive at 1000/T = 1.002 (997 K) consistent with crossing a eutectic temperature. The eutectic and maximum melting points are almost degenerate. There seems to be general agreement on the position of the Te-rich solidus of the $GeTe(c)$ phase, for which a significant number of points originate from these optical density measurements. However, there is sharp disagreement on the composition at the maximum melting point.[6,7] Chemical analysis of the first and last to freeze of directionally frozen ingots and related thermal cooling curves[6] indicated a Ge- $GeTe$ eutectic at 997 K and 49.84 at.% Te. However, they also found the composition of the first part of a directionally frozen 50.00 at.% Te ingot was 50.60 at.% Te, which was taken as the composition at the maximum melting point. The reason for this discrepancy in the composition for the maximum melting point is not understood. A number of experiments have been carried out to establish the solidus lines for $GeTe(c)$ and a summary of these has been given.[23] Most of the experiments have been carried out at low temperatures where the high-temperature beta phase is no longer stable and therefore refer to the alpha and gamma phases. In one exception, crystals are grown at 973 and 827 K from the vapor phase over 50.30 at.% Te starting material.[24] It is observed that Ge crystals are found on the surface of the last portion grown. A composition for the $GeTe(c)$ grown from the vapor is calculated from the initial weight and composition and the weight of $Ge(c)$ rather than being determined directly. This ranges from 50.65 at.% Te for a 973 K growth temperature to 50.58, 50.44, and 50.34 at.% Te for growth temperatures at respectively, 926, 874, and 827 K. These findings are claimed to indicate a maximum melting point at 50.60 at.% Te. However, the occurrence of $Ge(c)$ at the end of the vaporization process is due to the fact that the vapor includes $Te_2(g)$ as well as $GeTe(g)$ so $Ge(c)$ remains at the last stages of the vaporization. Moreover, the growth of a crystal at some temperature from a source at another higher temperature is not the same as equilibrating $Ge(c)$ and $GeTe(c)$ at the same temperature, as seems to have been assumed. Therefore it is not clear to us the conclusions drawn concerning the solidus curve are correct. In another study[25] high-temperature x-rays have been taken of compositions every .1 at.% between 49.8 and 51.0 at.% Te and every .2 at.% between 51 and 52.6 at.%. Samples were heated under He pressure in quartz capsules at 1173 K for 20 min and then cooled slowly in the furnace. They were then annealed for 120 h at 873 K, 14 h at 773 K, and 170 h at 693 K. Other anneals were made at lower temperatures in a study of the low temperature alpha and gamma phases that are not of interest here. Plots of lattice parameter versus at.% Te isotherms showed a constant value at the lower concentrations, then decreased linearly with increasing Te concentration, and finally became constant at a lower value. The transition points from constant to linearly changing value marked the composition of solidus points. At 873 K the solidus points were 50.20 and 51.50 at.% Te. At 773 K they occurred at 50.27 and 51.60 while at 693 K they occurred at 50.47 and 51.30 at.% Te. The Te rich solidus points are close to our values.[6,7] However, on the Ge rich side they seem to be more consistent with a 50.60 at.% Te maximum melting point. The only experiments we are aware of besides ours that gave a

solidus point at less than 50 at.% Te are the metallographic analysis, microhardness and DTA measurements[14] made on 15 different compositions between 49.4 and 51.8 at.% Te. They gave solidus points at 729, 711, and 709 K as, respectively, 49.4, 50.0, and 50.1 at.% Te. With these results the authors drew a T–X diagram with a maximum melting point at 50.1 at.% Te. There were no experimental points at these high temperatures so the choice of 50.1 seems somewhat arbitrary but perhaps more reasonable on the basis of their results than 50.6 at.% Te.

Gibbs Energy of formation of $\mathrm{GeTe(c)}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ for Compositions Within the $\mathrm{GeTe(c)}$ Homogeneity Range

To obtain the Gibbs energy of formation of $\mathrm{GeTe(c)}$ for compositions within its homogeneity range we start with the Gibbs–Duhem equation written in terms of the system chemical components,

$$(1-\mathrm{X})\mathrm{d}_{\mu_{\mathrm{Ge}}} + \mathrm{X}\mathrm{d}_{\mu_{\mathrm{Te}}} = 0 \text{ constant T and P}$$

(33)

Since the chemical potential of $\mathrm{Ge(c)}$ equals that of $\mathrm{Ge(g)}$ in the equilibrium vapor phase, similarly the chemical potential of $\mathrm{Te(l)}$ equals one-half that of $\mathrm{Te_2(g)}$, and since we assume an ideal vapor, Eq 33 can be written as

$$\mathrm{d}\ln \mathrm{P}_{\mathrm{Ge}}/\mathrm{dX} = \frac{(0.5\mathrm{X})}{(1-\mathrm{X})}\mathrm{d}\ln \mathrm{P}_{\mathrm{Te}_2}/\mathrm{dX}$$

(34)

Isotherms of $\ln \mathrm{P}_{\mathrm{Te}_2}$ versus X were constructed from the least squares fit values of $\ln \mathrm{P}_{\mathrm{Te}_2}$ versus 1000/T. A least squares line which was constrained to fit the point for Ge saturated $\mathrm{GeTe(c)}$ at 49.94 at.% Te exactly was obtained for each isotherm i.e.

$$\ln\left(\mathrm{P}_{\mathrm{Te}_2}\right) = \mathrm{A}(\mathrm{X}-.4984) - \ln\left(\mathrm{P}_{\mathrm{Te}_2}[\mathrm{X}=.4984]\right)$$

(35)

For four temperatures between 885 and 952 K the standard deviation of the fit to the natural logarithm of the pressure is between .24 and .27. The parameter A varies from 274 and 187. With Eq 35 for the logarithm the differentiation on the right side of Eq 34 could then be carried out and the equation integrated to obtain the pressure of germanium as:

$$\ln \mathrm{P}_{\mathrm{Ge}} = \ln \mathrm{P}^{\mathrm{o}}_{\mathrm{Ge}} + .5\mathrm{A}\left(\mathrm{X}-.4984+\ln\left(\frac{1-\mathrm{X}}{1-.4984}\right)\right)$$

(36)

Here $\mathrm{P}^{\mathrm{o}}_{\mathrm{Ge}}$ is the vapor pressure of $\mathrm{Ge(c)}$ whose natural logarithm is given by Eq 11. Calculations were made at 885, 901, 934, and 952 K. The Gibbs energy of formation of $\mathrm{Ge}_{1-\mathrm{X}}\mathrm{Te}_{\mathrm{X}}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ was then calculated and the isotherms are shown in Fig. 6. It can be seen that the Gibbs energy of formation becomes more negative with increasing atom fraction of tellurium but varies by less than 100 J/g-atom between 49.94 and 51.01 at.% Te.

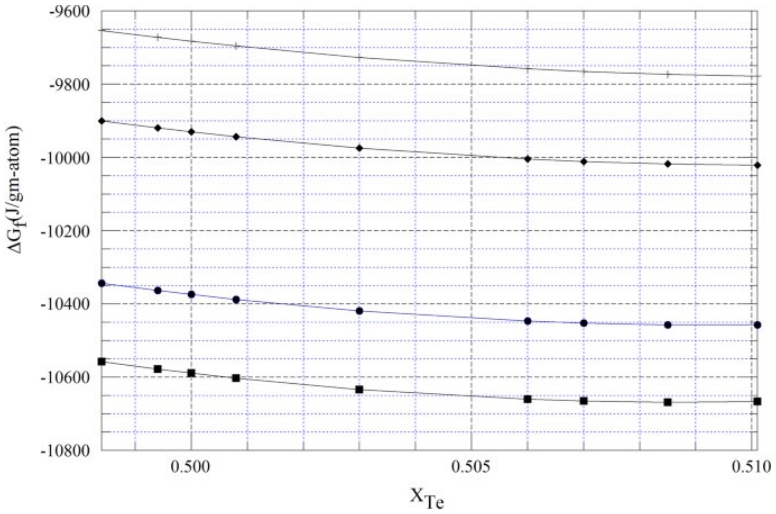

Fig. 6 Isotherms of the Gibbs energy of formation of $Ge_{(1-X)}Te_X$ (c) from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ in J/g-atom. From top down the temperatures are 952,923, 901, and 885 K. X is the atom fraction Te

Modeling of the $\mathrm{Ge-Te}$ system by Schlieper et al.[23] has fit extensive enthalpy and phase diagram data. As far as we can discern, their results for the Gibbs energy of formation of $Ge_{1-X}Te_X$(c) are incomplete in that a value for the standard enthalpy of formation at 298 K is not given. However, this parameter cancels out in the difference in the standard Gibbs energy of formation for different compositions so some comparison with the present results can be made. Their difference for 50.3 and 51.0 at.% Te compositions is 1200 J/g-atom at 800 K. The corresponding difference found here is one-tenth of that. They make no mention of the partial pressure measurements. Therefore, we have used thermodynamic formulae to extract the relative chemical potentials of Ge and Te from their equation for the Gibbs energy of formation of the beta phase of $Ge_{1-X}Te_X$(c). The chemical potentials depend on the Gibbs energy of formation at 298 K which is expected to be negative and to make the calculated partial pressure of $\mathrm{Te_2}$ smaller the more negative it is. If one takes the extreme, unrealistic, case that the Gibbs energy of formation at 298 K is zero then for 50.600 at.% Te and 900 K the calculated partial pressure of $\mathrm{Te_2}$ is ten orders of magnitude less than the observed[8] value of $3.3(10^{-4})$.

Further Effusion Measurements

The weight loss from an effusion cell into a pumped vacuum has been continuously measured.[26] The samples were taken from a boule grown under borax from a 50 at.% Te melt. A large part was single crystal while the last to freeze was polycrystalline and contained $\mathrm{Ge(c)}$ as a second phase. A number of effusion runs were made with about 50 mg of 200 mesh material. After an initial stage a near steady state was reached in which the weight of weight loss slowly decreased with time. A constant rate is expected for a composition within the Ge-GeTe-vapor field. A Ge residue was found in each case, the amount increasing with increasing effusion rate. Knowing the initial weight of GeTe, the weight of the Ge residue, assuming $\mathrm{GeTe(g)}$, $\mathrm{Te_2(g)}$, and $\mathrm{GeTe_2(g)}$ to be the vapor species, and taking the $\mathrm{Te_2}$/$\mathrm{GeTe_2}$ pressure ratio to be six from Colin and Drowart,[3] the mole fractions in the vapor could be calculated. It was concluded that presence of solid $\mathrm{Ge(c)}$ prevented the attainment of steady state conditions. To avoid this problem measurements were chosen immediately after the near steady state began when there was minimal composition change. Fifty four points from three runs between 729 and 872 K were obtained and a pressure calculated using the molecular weight of GeTe in the Knudsen equation. The average of the three runs gave

$$\ln \mathrm{P_{GeTe}(atm)} = -22{,}683/\mathrm{T} + 17.919 \tag{37}$$

From complete vaporization studies it was concluded that this apparent pressure was between 1.03 and 1.06 that of the actual pressure of $\mathrm{GeTe(g)}$. Figure 7 shows that our result from Eq 18 lies about 10% higher than that from Eq 37. The line terminated by circles also is close to coinciding with the other two and is from the torsion and effusion cell studies of Ferro et al.[27] discussed below, The bottom line is our result for the partial pressure of diatomic tellurium over Ge saturated $\mathrm{GeTe(c)}$ given by Eq 10.

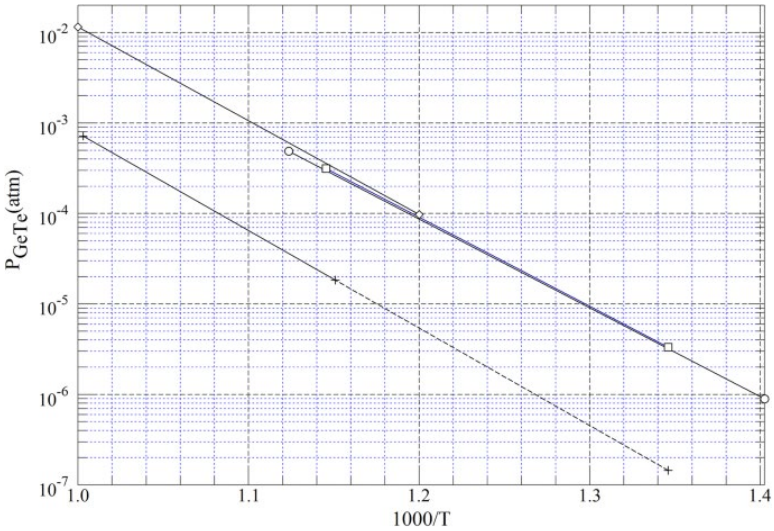

Fig. 7 Partial pressure of $\mathrm{GeTe(g)}$ over Ge-saturated GeTe. Line terminated by diamonds is from this work. Line terminated by circles from Ref 27. Line terminated by squares is from Ref 26. Lowest line is our partial pressure of tellurium over Ge-saturated $\mathrm{GeTe(c)}$

Four torsion cell and two Knudsen effusion cell runs were made[27] between 713 and 893 K. Vapor pressures were calculated assuming $\mathrm{GeTe(g)}$ to be the only vapor species. Readings were taken only at the first stage at which the weight vaporized was 2-3 wt.% of the initial weight similar to Northrop' procedure.[26] No description of the GeTe samples was provided but presumably they were 50 at.% and quickly reached a state in which the surface layer was Ge saturated. Tellurium was not detected. The average $\mathrm{GeTe(g)}$ partial pressure is given by,

$$\ln \mathrm{P_{GeTe}(atm)} = -22{,}611 \pm 690/\mathrm{T} + 17.832 \pm 1.15$$

(38)

which is plotted in Fig. 7. As mentioned above it is in close agreement with Northrop's value[26] and extends closely to our result at higher temperature. Presumably Northrop's description of the effusion process given above is more correct than that of the author's.

Partial Pressures of $\mathrm{GeTe(g)}$ for Compositions Within the $\mathrm{GeTe(c)}$ Homogeneity Range

Least squares fits were obtained to $\mathrm{Ln(P_{GeTe})versus1000/T}$ for compositions within the homogeneity range of $\mathrm{GeTe(c)}$. Since these pressures vary with composition by about a factor of two or less, isotherms were constructed to show the relative values of the pressures more clearly. These isotherms are shown in Fig. 8 as open circles. The observed variation with composition is irregular and the pressure varies over a wider range than is shown by a Gibbs–Duhem integration as shown below. They reach a minimum value for each temperature around 50.30 and 50.60 at.% Te. In our earlier publications[7,8] these pressures were considered to be the same within experimental error. One can obtain an alternate set of values for the partial pressure of GeTe as follows. Replacing the chemical potential of Te by that of $\mathrm{Te_2(g)}$ and that of Ge by those of $\mathrm{GeTe(g)}$ and $\mathrm{Te_2(g)}$ the Gibbs–Duhem relation becomes,

$$(1 - \mathrm{X})\mathrm{d}\mu_{\mathrm{GeTe}} + (\mathrm{X} - .5)\mathrm{d}\mu_{\mathrm{Te}_2} = 0 \text{constant T and P},$$

(39)

where X is the atomic fraction of tellurium. Assuming the vapor is ideal the chemical potentials can be written in terms of the logarithm of the corresponding partial pressures and the equation rearranged to give,

$$\frac{d \ln \mathrm{P}_{\mathrm{GeTe}}}{dX} = \frac{\left(X - \frac{1}{2}\right)}{(1 - X)} \frac{d \ln \mathrm{P}_{\mathrm{Te}_2}}{dX}$$

(40)

According to Eq 40, the partial pressure of $\mathrm{GeTe(g)}$ is an extremum, which turns out to be a maximum, at X = .5 and decreases monotonically with increasing X from X = .5 for a stable phase. Figure 8 shows this requirement is not met by the experimental partial pressures of $\mathrm{GeTe(g)}$ for all of the compositions. Equation 35 in section 4.5 was used again for the partial pressure of tellurium allowing the right side of Eq 40 to be written as an analytical expression. Integration of Eq 40 then gives,

$$\ln(\mathrm{P}_{\mathrm{GeTe}}/\mathrm{P}^{\mathrm{o}}_{\mathrm{GeTe}}) = \mathrm{A}(\mathrm{X} - .4984) + (\mathrm{A}/2)\ln\left(\frac{1 - \mathrm{X}}{1 - .4984}\right)$$

(41)

where $\mathrm{P}^{\mathrm{o}}_{\mathrm{GeTe}}$ is the partial pressure over Ge saturated $\mathrm{GeTe(c)}$ given by Eq 18. The diamonds in Fig. 8 show the results for 952 and 885 K. The partial pressures decrease with increasing atom fraction of tellurium greater than ½ but vary by less than 2.5%. Secondly, the partial pressures are in fairly close agreement with the values from the partial optical densities shown as circles at atom fractions of 50.00 and 50.70 at.% Te. At the other compositions they are 17-67% high. The reason for this larger than expected experimental discrepancy in the measured partial pressures of $\mathrm{GeTe(g)}$ in this middle range is unknown. The optical densities at 320 and 330 nm from which they are derived are measured in the same spectral scans as the optical density at 435.7 nm used to determine the partial pressure of tellurium.

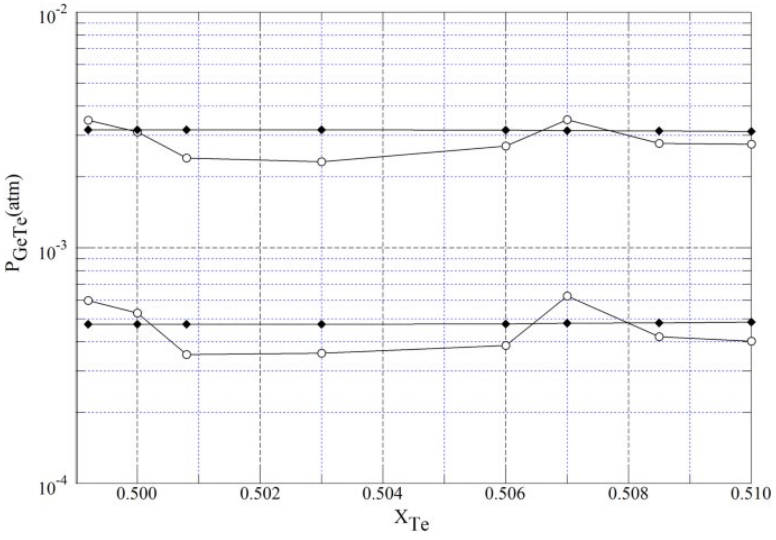

Fig. 8 Isotherms of the partial pressure of $\mathrm{GeTe(g)}$ over $Ge_{1-x}Te_x$(c) as a function of the atom fraction of Te. Circles are from the partial optical density of $\mathrm{GeTe(g)}$. Diamonds are from integration of the Gibbs–Duhem relation over the partial pressure of $\mathrm{Te_2(g)}$. Upper pair of curves are for 952 K. Lower pair are for 885 K

Values of the partial pressure of GeTe for 50 at.% Te are available for four temperatures between 1012 and 1047 K above the melting point as well as eleven temperatures between 884 and 994 K below as shown in Fig. 9. The pressures are calculated from the partial optical densities at 320 and 330 nm and are in close agreement or, above the melting point, the same. Moreover, as seen in Fig. 8 these partial pressures are in close agreement with those calculated integrating over the $\mathrm{Te_2}$ pressure. This leads us to conclude they are reliable so least squares fits are made to obtain a value for the enthalpy of fusion. The fits are:

$$\begin{aligned} \ln P_{\mathrm{GeTe}} &= -23{,}000 \pm 600/\mathrm{T} + (18.3 \pm .6)\mathrm{T} \leq 997\mathrm{K}\ \sigma = .05 \\ \ln P_{\mathrm{GeTe}} &= -17{,}000 \pm 600/\mathrm{T} + (12.3 \pm .5)\mathrm{T} \geq 997\mathrm{K}\sigma = .008 \end{aligned}$$

(42)

The difference in slope is 6030 which when multiplied by the gas constant 8.3145 gives 50,130 J/mol of $\mathrm{GeTe(c)}$ as the enthalpy of fusion. A value of 42,030 J/mol has been obtained by drop calorimetry.[28] Another drop calorimetry measurement[29] using a Calvet calorimeter was used to measure the enthalpy of solid and liquid GeTe between 550 and 1300 K, giving an enthalpy of fusion of 39,400 J/mol of GeTe. Finally, pieces of Te at 298 K were added to a calorimeter containing $\mathrm{Ge(c)}$ at temperature T in a Tian–Calvet calorimeter.[30] The standard enthalpy of formation of liquid GeTe from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ was determined as a function of temperature. Its value at 997 K is 6284 J/mol for 50 at.% Te. Combining our value of 50,130 J/mol for the enthalpy of fusion for GeTe with our value of − 44,994 J/mol for the enthalpy of formation of solid GeTe at 997 K from Eq 30 gives an enthalpy of formation of liquid GeTe from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ of 5146 J/mol in fair agreement with the value of 6284 J/mol. The above procedure discounts enthalpy measurements on the solid.[30] If they are accepted one has 6284 J/mol for the enthalpy of formation of the 50% liquid as before, 37,880 J/mol for the enthalpy of fusion, and then − 31596 J/mol follows as the enthalpy of formation of $\mathrm{GeTe(c)}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ compared to our value of − 44,944 J/mol from Eq 30.

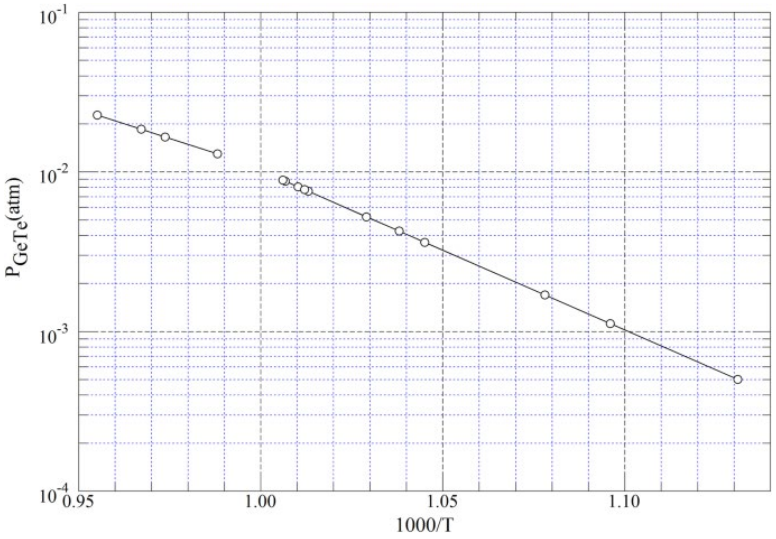

Fig. 9 Partial pressure of $\mathrm{GeTe(g)}$ over 50.00 at.% Te GeTe solid and liquid. Partial pressure obtained from the optical densities at 320 and 330 nm with tellurium corrections using the optical density at 435.7 nm

Summary

We have reexamined our earlier measurements of the optical density of the vapor at 1000 °C from $Ge_{1-x}Te_x$(c) at various lower temperatures. Equations expressing the optical density at various wavelength pairs in terms of partial optical densities of $\mathrm{Te_2(g)}$ and $\mathrm{GeTe(g)}$ are derived. The dependence of the optical density of $\mathrm{GeTe(g)}$ upon wavelength between 320 and 500 nm is obtained from measurements with a 1 at.% Te sample at temperatures above the melting point of Ge. This is at temperatures higher than used before and where the spectrum is more likely to be solely that of $\mathrm{GeTe(g)}$. The Beers law constants for $\mathrm{GeTe(g)}$ are obtained from measurements on 1 and 49.84 at.% Te samples, which are in the $\mathrm{Ge(c)}$-Ge saturated $\mathrm{GeTe(c)}$-vapor field below 997 K, by considering the dissociation of $\mathrm{GeTe(g)}$. The partial pressure of $\mathrm{Te_2(g)}$ is obtained from its partial optical density using published Beers law constants. The partial pressure of $\mathrm{Ge(g)}$ is taken as equal to the vapor pressure of $\mathrm{Ge(c)}$ because of the small, less than 1 at.%, solubility of Te in $\mathrm{Ge(c)}$. The partial pressure of $\mathrm{GeTe(g)}$ is taken as the product of an unknown Beers law constant and the partial optical density of $\mathrm{GeTe(g)}$. Requiring agreement with spectroscopic results for the entropy of dissociation of $\mathrm{GeTe(g)}$ yields the $\mathrm{GeTe(g)}$ Beers law constants. The partial pressure of $\mathrm{GeTe(g)}$ over Ge-saturated $\mathrm{GeTe(c)}$ is compared with those from a number of effusion studies at this point and later in the discussion. The Gibbs energy of dissociation of $\mathrm{GeTe(g)}$ into $\mathrm{Ge(g)}$ and $\mathrm{Te_2(g)}$ is obtained. Then the Gibbs energies of formation between 870 and 997 K of Ge-saturated $\mathrm{GeTe(c)}$ from $\mathrm{Ge(c)}$ and $\mathrm{Te_2(g)}$ as well as from $\mathrm{Ge(c)}$ and $\mathrm{Te(l)}$ are calculated. The enthalpy and entropy of formation at 298 K for the latter is obtained by a second law analysis and compared with other published results. The Gibbs energies of formation of $\mathrm{GeTe(c)}$ for compositions within the homogeneity range are obtained from the partial optical density of $\mathrm{Te_2(g)}$ and partial pressures of $\mathrm{Ge(g)}$ obtained by integration of the Gibbs–Duhem relation and found to vary by 100 J/mol or less between 49.94 to 51.5 at.% Te for temperatures between 885 and 952 K. Partial pressures of $\mathrm{GeTe(g)}$ constant to within 2.5% across the homogeneity range are obtained by integration of the Gibbs–Duhem relation written in terms of GeTe and $\mathrm{Te_2}$ as components and

integrated over known values of the latter. For unknown reasons the partial pressures obtained from the partial optical densities of $\mathrm{GeTe(g)}$ are somewhat lower and differ by more than expected, especially at 50.3 and 50.6 at.% Te. The values from both sources are in agreement for 50 at.% Te and include measurements above the melting point. Least squares fits are made and lead to an enthalpy of melting of 50,030 J/mol, somewhat higher than literature values. The partial pressures of $\mathrm{Te_2(g)}$ are essentially unchanged from their older values. They are shown along the three phase curves for $\mathrm{Ge(c)}$ and $\mathrm{GeTe(c)}$ and for some compositions within the $\mathrm{GeTe(c)}$ homogeneity near 50 at.%. The implications of these latter measurements for the structure of the phase diagram are discussed.

Finally, the partial pressures obtained here show there is no congruently subliming composition for $\mathrm{GeTe(c)}$. The vapor phase is richer in Te than the coexisting solid. Between 700 and 950 K the vapor over 50 at.% Te solid ranges between 50.95 and 52.10 at.% Te. Over 50.30 at.% Te the vapor is close to 53.40 at.% Te over the whole temperature range. Thus the surface layer of a vaporizing solid becomes richer in Ge and solid state diffusion is required to maintain equilibrium. However, for compositions within the $\mathrm{Ge(c)}$- $\mathrm{GeTe(c)}$-vapor three phase field continued vaporization requires only a surface change in the amounts of the two solid phases. It would seem equilibrium should be more easily maintained for compositions including Ge-saturated $\mathrm{GeTe(c)}$ and Te-saturated $\mathrm{Ge(c)}$. If so then the partial pressures of $\mathrm{Te_2(g)}$ and $\mathrm{GeTe(g)}$ measured for these compositions and the Gibbs energies obtained from these partial pressures would be more likely to be representative of equilibrium then those for other compositions within the homogeneity range for $\mathrm{GeTe(c)}$. Assuming the $GeTe_2$ species has a partial pressure one tenth that of $\mathrm{Te_2}$ leaves the above results essentially unchanged.

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